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(54) UV curable epoxysilicones.

(57) A UV curable epoxysilicone blend of an epoxy functional silicone resin containing Q groups, epoxy functional M groups, and at least one member selected from D groups and T groups, at least 5 parts of the sum of M groups and epoxy functional M groups per 10 parts of the sum of Q groups, D groups and T groups; and an epoxy-stopped silicone fluid containing epoxy functional M groups.

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BACKGROUND OF THE INVENTION

Curable silicone coatings for release of pressure-sensitive adhesives (PSA) are known. These coatings may be cured via tin-catalyzed condensation reactions, platinum-catalyzed addition reactions, or radiation-initiated crosslinking reactions.

Linear polydimethyl siloxanes form what are referred to as premium or low release coatings. When cross-linked, these materials form adhesive surfaces from which a PSA-laminated facestock may be detached with very little force required. Such premium release characteristic is desirable for many applications.

There are, however, significant applications for silicone release coatings which do not provide easy release from PSA's. Such coatings which provide a tight or controlled release characteristic are desirable, for example, in industrial labeling operations which run at high speed. A high release silicone agent is desirable in order to prevent so-called premature dispensing of the label from the release liner. A controlled release characteristic is useful for two-sided release laminate applications wherein one side of the laminate is coated with a premium release silicone and the other side is coated with a tight release silicone, thus providing a differential release structure.

Ideally, silicone release systems that have a range of release characteristics are desirable. Such silicone coating systems would enable an end-user to selectively adjust the formulation to give the desired level of release depending on the specific application. A tight release polymer capable of giving a range of release levels in a blend with premium release polymer is referred to as a controlled release additive (CRA).

Despite the intensity of effort in this area, commercial products designed to be controlled release (tight release) additives (CRAs) for ultraviolet radiation curable epoxysilicone release systems have not been generally successful because they often do not cure as readily as the premium release epoxysilicones; they do not provide large release differential vs. the premium release materials except at very high concentrations in coating baths (>70%); and cured films containing these CRAs often lose their high release characteristics as they age after cure. Promising experimental UV-curable CRAs have also not been as efficient as desired, and in many cases have caused undesirable 'zippy' (jerky, uneven) type release which is unacceptable in the market.

Exemplary UV-CRA products provide tight release (relative to the premium release epoxysilicone polymers taught in U.S. Patent No. 4,279,717 and other patents) by incorporation of highly polar hydroxybenzoate ester groups (U.S. Patent No. 4,977,198) or phenol groups (U.S. Patent No. 4,952,657) along with reactive epoxy groups into the polydimethylsiloxane polymers. In each case, products so designed are not successful for reasons noted above.

UV-CRAs incorporating reactive, epoxy-functional 'Q' type silicone resins plus linear (nonresinous) epoxysilicone polymers analogous to traditional thermally cured silicone CRAs (solvent-borne and solventless) which make use of silicone resins as taught in U.S. Patent Nos. 4,123,604, 3,527,659 and 5,158,911 and in U.S. patent application serial no. 07/923,112, filed July 30, 1992, in the name of Eckberg and Griswold. In U.S. Patent No. 5,158,911, the epoxy-MQ resins taught therein are high viscosity (or solid) materials incompatible with low viscosity epoxysilicone carriers without solvent vehicle. Eckberg and Griswold, which teaches 'bound' M'TQ resin/epoxysilicone fluid compositions, is limited in effectiveness because solventless silicone coating constrains coating bath viscosities to be <1000 cstk, which in turn limits the actual resin content of the CRA <35 wt %. High release of these materials is a function of actual epoxysilicone resin concentration. Thus, the efficiency of the compositions is limited.

SUMMARY OF THE INVENTION:

The present invention is based upon the discovery that certain unique combinations of epoxy-functional silicone resins plus epoxy-terminated dimethylsilicone fluids overcome the performance deficiencies associated with the UV cure epoxysilicone CRAs noted above. Improved CRA performance lies in careful matching of epoxy content of the resin with that of the epoxy-stopped fluid, plus formulating epoxysilicone resins including D groups with TQ- or Q-containing resins also including sufficient M (as M and M^E) to keep the resin + fluid compositions coatable at 100% silicone solids even when the resin component of the complete CRA exceeds 50 wt %.

In a particular embodiment, the invention is directed to an ultraviolet radiation-curable epoxysilicone composition comprising a blend of epoxy-functional silicone resins and epoxy-stopped silicone fluids curable in the presence of an efficacious amount of 'onium-type cationic photocatalyst and ultraviolet radiation. Exemplary 'onium catalysts include iodonium and sulfonium salts. The blend comprises: (A) from about 20 to about 80 % by weight epoxy-functional silicone resin, said resin containing Q groups, epoxy-functional M groups and at least one member selected from D groups and T groups at least 5 parts of the sum of M groups and

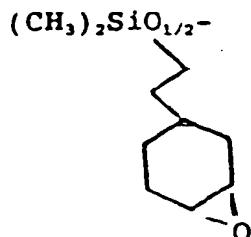
epoxy-functional M groups per 10 parts of the sum of Q groups, D groups and T groups; and (B) about 80 to about 20 % by weight epoxy-stopped silicon fluids containing epoxy-functional M groups; the blend (A) and (B) having an epoxy equivalent weight of greater than 1000.

In the epoxysilicone composition an effective epoxy-functional M group is

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DESCRIPTION OF THE INVENTION:

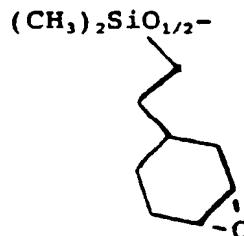
20 The present invention is directed to an ultraviolet radiation-curable epoxysilicone composition which is a blend of epoxy-functional silicone resins and epoxy-stopped silicone fluids which may be cured to an adhesive coating in the presence of an efficacious amount of photocatalyst and ultraviolet radiation. The blend generally comprises (A) from about 80 to about 20 % by weight epoxy-functional silicone resin, said resin containing Q groups, epoxy-functional M groups and at least one member selected from D groups and T groups, at least 5
25 parts of the sum of M groups and epoxy-functional M groups per 10 parts of the sum of Q groups, D groups and T groups, and (B) about 20 to about 80 % by weight epoxy-stopped silicone fluids containing epoxy-functional M groups, said blend having an epoxy equivalent weight of greater than 1000.

In the epoxysilicone composition an effective epoxy-functional M group is

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In a particular embodiment, the ultraviolet radiation-curable epoxysilicone composition comprises a blend of epoxy-functional silicone resins and epoxy-stopped silicone fluids curable a weight percent ratio of 60:40. The composition is curable in the presence of an efficacious amount of photocatalyst and ultraviolet radiation.

45 For purposes of this disclosure, the following abbreviations will be employed:

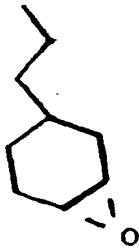
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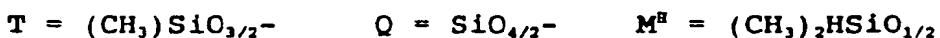


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Other aliphatic or aromatic radicals having 2 to about 10 carbon atoms may be substituted for (CH_3) .
The following are the general procedures for making the SiH-functional resin and fluid UV-CRA precursors.

SiH-Stopped Resin Solution:

A xylene solution of the following silanes was prepared:

1.0 part dimethylchlorosilane, 9.4 parts trimethylchlorosilane, 4.2 parts dimethyldichlorosilane, 2.9 parts trimethoxymethylsilane, and 11.3 parts tetraethylorthosilicate $(EtO)_4Si$. The mole ratio of these silanes were approximately 1:8:3:2:5 M^H:M:D:T:Q. This solution was slowly added to 40 parts water at 10-30°C over a 60 minute period, then agitated for two more hours at 40°C. The organic phase was separated from the aqueous phase, the aqueous phase discarded, the organic phase then refluxed at 130-140°C using a Dean-stark apparatus to remove water, then finally raising the reflux temperature to 160°C at which point the resin was bodied and the solids content was 60%. Analysis of the resin solution indicated @ 700 ppm H (as reactive M^H), with Si²⁹ analysis confirming the resin formula to be @ $M^H M_8 D_3 T_2 Q_5$. Other resins to be described in the disclosure were made in this fashion. We found that removal of all xylene solvent from this solution resulted in isolation of a solid, water-white silicone which softened and readily flowed when warmed above 70°C. Isolation of the SiH resins was not necessary, however, and their xylene solutions were used to make the final UV-CRA compositions.

SiH-Stopped Silicone Fluid:

This material was prepared via standard acid-catalyzed equilibration of octamethylcyclotetrasiloxane, D₄, with 1,1,3,3-tetramethyldisiloxane, M^HM^H. Sulfuric acid/carbon black catalyst (0.1% acid) was used to equilibrate 163 grams D₄ with 14 grams M^HM^H. The final product was a 20 cstk viscosity fluid, 859 ppm H (as SiH) per gaseometric analysis, including 17% volatiles. The approximate formula, based on the SiH analysis, was M^HD₂₉M^H. Other SiH-stopped (dimethylsilyl-stopped) linear polydimethylsiloxanes to be mentioned in this disclosure were made and characterized in the same fashion.

UV-Curable Epoxysilicone CRA Compositions:

Example 1

100 parts of the SiH resin solution (@ 60 parts of resin solids) plus 40 parts of the SiH-stopped silicone fluid were mixed together with 0.01 part methylidicocoamine stabilizer and sufficient $RhCl_3(Bu_2S)_3$ catalyst (as an 11% solution in ethanol) to provide @ 3 ppm rhodium to the reaction mixture. 14 grams 4-vinylcyclohexene oxide (VCHO) were added, the reaction mixture then brought to 110°C. An exothermic response occurred which raised batch temperature to 140°C. SiH was undetectable after 2 hours' hold at 120°. Stripping off xylene, excess VCHO, and siloxane light ends in vacuo afforded a clear fluid product, 450 cstk viscosity and 96% solids, which included about 60 wt % epoxy-functional resin $M^E M_8 D_3 T_2 Q_5$ plus 40 wt % epoxy-stopped

fluid M^ED₂₉M^E. Various materials listed below in Table 1A were made in this same fashion. An amine/rhodium catalyzed addition of VCHO to the mixture of SiH-functional silicones as taught by Eckberg and Agars, U.S. patent application serial no. 07/802,681, filed December 5, 1991 (incorporated herein by reference) was employed.

Several complete UV-CRA candidate materials were produced using different SiH resin and SiH-stopped fluid inputs. In all cases VCHO addition proceeded smoothly and the resulting products were readily isolated and characterized. The results are tabulated below:

TABLE 1A

EXAMPLE	RESIN	FLUID	RESIN/FLUID
1	M ^E ₃ M ₆ T ₅ Q ₅	M ^E D ₁₀ M ^E	60/40
2	M ^E _{1.5} M ₃ T ₅ Q ₅	M ^E D ₁₀ M ^E	60/40
3	M ^E ₃ M ₆ T ₅ Q ₅	M ^E D ₁₀ M ^E	70/30
4	M ^E ₃ M ₆ T ₅ Q ₅	M ^E D ₅₀ M ^E	60/40
5	M ^E ₂ M ₇ T ₅ Q ₅	M ^E D ₅₀ M ^E	70/30
6	M ^E M ₈ T ₅ Q ₅	M ^E D ₂₂ M ^E	60/40
7	M ^E M ₈ T ₄ Q ₆	M ^E D ₅₄ M ^E	60/40
8	M ^E M ₈ D ₅ Q ₆	M ^E D ₂₉ M ^E	60/40
9	M ^E M ₈ D ₃ T ₂ Q ₅	M ^E D ₂₉ M ^E	60/40
10	M ^E M ₈ D ₂ T ₃ Q ₅	M ^E D ₂₉ M ^E	60/40
11	M ^E M ₈ DT ₄ Q ₅	M ^E D ₂₉ M ^E	60/40

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TABLE 1B

<u>EXAMPLE</u>		<u>APPEARANCE</u>	<u>VISCOOSITY</u>	<u>E.E.W.^{**}</u>
5	1	Clear Fluid	373 cstk	600
	2	Clear Fluid	16400	680
	3	Clear Fluid	972	600
10	4	Hazy-two phases resin settled out		
	5	Hazy-resin phase separated out		
15	6	Clear Fluid	1024	990
	7	Hazy - resin phase separated out		
	8	Clear Fluid	250	1100
20	9	Clear Fluid	450	1100
	10	Clear Fluid	635	1100
	11	Clear Fluid	500	1100
25	* All samples cited above were > 96% solids per 150°C, 45 min. weight loss testing			
	** Calculated Epoxy Equivalent Weight			

It appears that coatable epoxysilicone resin/fluid mixtures (neat viscosity <1000 cstk) with resin content 30 >50% require that total 'M' in the resin be at least 50 mole percent of total ('D' + 'T' + 'Q'), preferably 75-100 mole percent. It is also important that the epoxy content of the epoxysilicone resin be comparable to, or less than the epoxy content of the epoxy-stopped silicone fluid component of the CRA composition or else the two parts of the CRA are immiscible and will not form a stable clear blend.

Several examples from the initial CRA formulations in Examples 1 - 11 above were selected which met 35 convenient criteria for stability and coatable viscosity. These were prepared for assessment as 0.5 mil coatings on Polyethylene Kraft (PEK) liner stock when blended neat with 1 wt % iodonium catalyst $(C_{12}H_{25}Ph)_2ISbF_6$ in 2 ethyl 1,3 hexane diol, 50% active ingredients. An RPC Model QC1202 Lab UV Processor equipped with two medium pressure mercury vapor ultraviolet lamps was used.

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TABLE 2

<u>Example</u>	<u>Appearance</u>	<u>UV Flux for Cure*, mJ/cm²</u>
1	clear mix	20
3	clear mix	40
6	slightly hazy, stable	40
8	hazy, but no separation	42
9	hazy mixture, stable	45
10	hazy mixture, stable	50
11	hazy mixture, stable	45
12**	clear mix	20
13***	clear mix	68

* 'cure' defined as smear- and migration-free (vs 3M Scotch 610 tape) silicone coating.

** control, easy release epoxysilicone, i.e., linear epoxy functional silicone fluid having an EEW of about 900 and a nominal viscosity of about 300 cstk at 25°C

*** control, tight release epoxysilicone, i.e., linear polymer containing substantially equal amounts of epoxy functional groups and phenol functional groups, and the balance being dimethyl siloxane functional groups, having an EEW of about 1500 and a nominal viscosity of about 300 cstk at 25°C

UV-CRA formulations with highest epoxy content were most compatible with the iodonium catalyst and generally gave the most efficient cure (lowest UV flux needed for cure). Even where the catalyst was not completely miscible, coating baths tested showed no sign of physical separation of photocatalyst for several days after being blended. UV cure response of all these compositions was judged to be adequate, and in all cases was superior to that of the neat tight release polymer Example 13.

The selected materials were assessed as tight release additives in Example 12. Baths consisting of 75 parts of various high release candidates + 25 parts of Example 12 low release polymer were prepared, then mixed with 1 part of the iodonium photocatalyst, coated to @ 0.8 g/m² weight on PEK using a lab solventless coating device, and cured to migration-free coatings by exposure to @ 100 mJ/cm² UV flux in the RPC Processor. A control bath consisting of Example 12 alone was similarly catalyzed, coated, and cured. Test tape #4970 (an acrylic adhesive tape) was affixed to the silicon surface, and the taped release liners aged

at 70° for 20 hours. The force required to peel away the Tesa tape from the silicone surface at 180°, 50 inch/min. peel was determined as gram/inch (Tesa tape is 1 inch wide). The results of this experiment are given below:

TABLE 3

	EXAMPLE	RESIN FORMULA	RELEASE	REMARKS
	1	60% M ^E ₃ M ₆ T ₅ Q ₅	75-95 g/in.	zippy
10	3	70% M ^E ₃ M ₆ T ₅ Q ₅	110-130	very zippy
	6	60% M ^E M ₈ T ₅ Q ₅	115->250	very zippy
	8	60% M ^E M ₈ D ₅ Q ₅	110-140	smooth release
15	9	60% M ^E M ₈ D ₃ T ₂ Q ₅	150-215	smooth release
	10	60% M ^E M ₈ D ₂ T ₃ Q ₅	180-240	smooth release
	11	60% M ^E M ₈ DT ₄ Q ₅	250-300	sl. zippy release
20	12	(none)	25-30	smooth release

'Zippy' release, as defined previously, is considered undesirable for silicone release coatings, although MQ resin containing addition- and condensation-cure CRAs often display 'zippy' release at high CRA loads. Examples 1 and 9 were prepared in sufficient quantities to be run on an 18' wide 3 roll offset gravure 18 inch pilot coater equipped with two banks of Fusion Systems' microwave fired 'H' UV lamps capable of operation at 400 and 600 watts/inch nominal power. Initial experiments were carried out with the UV-CRA candidate Example 1 blended at various levels with the low or premium release epoxysilicone polymer Example 12 plus 1 wt % of the iodonium photocatalyst. These mixtures were coated on PEK substrate at a coat weight of @ 1.2 g/m², at a speed of 400 fpm, then exposed to the two banks of lamps set at 600 watts/in power. All coatings were cured to smear- and migration-free silicone surfaces immediately off line, with no evidence of post cure. Samples of the cured silicone liners so produced were maintained at room temperature for 6 days, then laminated with Monsanto Gelva 263 solvent-borne acrylic PSA, with a normal paper face stock applied to the adhesive. 2 inch wide tapes of these constructions were prepared, and the release force needed to pull the silicone/PEK lamina from the facestock/PSA lamina at 400 inch/min. pull speed and 180° determined periodically over a 4 week period. Release results are tabulated below:

TABLE 4

	Formulation	INITIAL	4 WK RELEASE	REMARKS
	% Ex. 1 in Ex. 12			
40	100%	25-60 g/2in	40-70 g/2in	very zippy
45	90%	25-50	35-65	very zippy
	80%	30-60	35-60	very zippy
	70%	30-60	35-55	very zippy
50	50%	25-45	30-50	slightly zippy
	0%	25-30	25-30	smooth release

The performance of the material of Example 1 proved to be unsatisfactory. Although the material coated and cured well, it provided only a small release differential vs the unmodified Example 12 or control baths, and also imparted an undesirable 'zippy' character to the release. This combination of poor CRA performance characteristics may result from the high epoxy content of the CRA composition. Eckberg (Radtech '88 North America Conference Proceedings, New Orleans, 1988) has shown that epoxy equivalent weight < 800 causes erratic, 'zippy' release in linear epoxysilicone release coatings. The results herein appear to reinforce this ob-

servation and extend the experiments to non-linear epoxysilicone resin/fluid compositions.

Example 9 materials were coated with premium release Example 12 on several different substrates using the offset gravure pilot coater referred to above. Coating baths consisting of Examples 9 and 12 blends with varying levels of Example 9 CRA, with a 1% load of the iodonium photocatalyst were made. Materials were coated on PEK at 400 fpm line speed, 1.2 g/m² coat weight as above, then laminated with the same Gelva 263 acrylic adhesive. Release results are noted below:

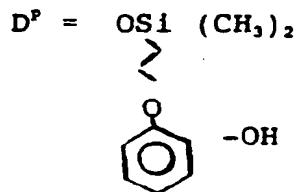
TABLE 5

	Formulation	Initial Release	4 Wk Aged Release	Remarks
	% Ex. 9 in Ex. 12			
10	100%	800 g/2in	850 g/2in	smooth release
15	90%	430	600	smooth release
20	80%	280	330	smooth release
25	70%	165	215	smooth release
	60%	105	135	smooth release
	50%	75	110	smooth release
	25%	55	65	smooth release
	0%	30	40	smooth release

Although release is slightly unstable over the 4 week period of these measurements, the large differential in release vs the unmodified control material of Example 12, even at fairly low levels of the CRA, coupled with the fact that even the highest release measured was not 'zippy', ragged or uneven, makes the performance of this material far superior to known epoxysilicone CRAs.

Comparative Example 14

A UV-CRA representative of prior art as taught in Riding, et al., U.S. Patent No. 4,952,657, approximate formula MD₁₅D^E₂D^P₂M, where D^E is as defined previously, and



Example 14 was blended with Example 12, catalyzed with 1% of the iodonium photocatalyst, then coated and cured on PEK using the same offset gravure pilot coater used for the evaluation of the new candidate UV-CRAs. Laminates with Gelva 263 were then prepared and release determined as described above. Typical results are as follows:

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TABLE 6

Formulation	Initial Release	4 Wk Release	Remarks
% Ex. 14 in Ex. 12			
90%	120 grams/2 in	125 g/2in	smooth release
50%	55	55	smooth release
0%	40	40	smooth release

This experiment demonstrates that the prior art UV cure epoxysilicone CRA of Example 14 does not provide as useful a release differential vs. the unmodified material of Example 12 as the UV CRA of Example 9.

Separate coating experiments with Example 9 UV CRA on the offset gravure pilot coater utilized different substrates and were tested with other adhesives. Some of the formulations coated on PEK were laminated using Ashland 1085 acrylic adhesive instead of the GELVA 263, with these results:

TABLE 7

FORMULATION	RELEASE, g/2in
% Ex. 9 in Ex. 12	
100% 475-1197	194
90% 475-1197	175
60% 475-1197	86
0% (UV9300)	39

Example 15

A premium release epoxy-silicone similar to Example 12 but with an EEW of 1100.

The Example 9 CRA was run as blends with Example 15 on high density polyethylene (3% catalyst was present in the coating formulations), 400 ft/min. line speed. The following release was recorded vs Gelva 263 adhesive:

TABLE 8

Formulation	Initial Release	3 wk Release
% Ex. 9 in Ex. 15		
80%	200 g/2in	215 g/2in
75%	115	120
50%	65	65
37.5%	45	50
25%	35	40
12.5%	35	40
0%	25	30

Similar formulations were coated on Kamm rer AV100 Glassine paper, at 200 fpm line speed. Release vs Gelva 263 PSA was the following:

TABLE 9

	Formulation	1 Wk Aged Release
	% Ex. 9 in Ex. 15	
5	90%	825 g/2in
10	80%	625
15	75%	470
	67%	370
	50%	200
	25%	100
	0%	55

These release results clearly demonstrate that the UV CRA composition of Example 9 is an efficient, useful UV curable tight release additive well designed for use with premium release epoxysilicone release polymers vs. different adhesives when applied to several different substrates. It is further demonstrated that significant differential release (compared to unmodified premium release baths) can be obtained by use of much less CRA than prior art epoxysilicone tight release additives require.

A sequence of experiments was carried out to determine if the tight release effect obtained with Example 9 (and analogous materials described herein) is stable; that is, if the cured silicone coating retains the high release desired as the cured coating ages. These evaluations were carried out as follows: cured samples of CRA-containing liner were set aside for 4 weeks after being coated, then laminated with Gelva 263 PSA; the laminates were measured for release after 4 weeks' aging, and the release values so obtained were compared with those from laminates prepared 6 days after coating (unlaminated liners were aged at room temperature). These results were obtained for blends of Example 9 and Example 12 formulations on PEK:

TABLE 10

	Formulation	6 Days Aged Liner	4 Wks Aged Liner
35	100%	850 g/2in	750 g/2in
	90%	610	520
	80%	340	350
40	70%	215	210
	60%	135	140
	50%	110	95
45	25%	65	55
	0%	40	35

Although some drop in release was observed after 4 weeks' aging of the unlaminated samples containing high levels of Example 9 CRA, the rest of the samples appeared to exhibit very stable release.

Comparative Example 16

Epoxy/phenol cofunctionalized silicone, approximate formula $MD_{20}DE_{1.5}DP_{1.5}M$ representative of known epoxysilicone CRAs (the same material described in comparative Example 14).

Another experiment relating to release stability of the unlaminated liners was carried out. In this case, PEK liners containing a CRA 90/10 blend of Example 9 with Example 15 coating and PEK-coated liners containing 100% of Example 16 were aged in a 70°C oven for 63 hours, then laminated with the Gelva PSA as

before. Release was determined one day after the laminates were prepared.

5 100% Ex. 14:	90% Ex. 9 in 10% Ex. 12: heat aged 650 g/2in heat aged 90 g/2in	not aged 740 g not aged 210 g
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10 While some drop in release is observed due to thermal aging of the Example 9 containing liner, this loss (@ 12%) is small compared to the dramatic > 50% decrease in release when the known Example 14 epoxy/phenol silicone CRA-coated liner is aged the same way.

15 The UV curable epoxysilicone compositions of the invention are well-suited for controlled release applications, and are superior to prior art materials for these purposes. These CRAs of the invention are blends of epoxy-functional silicone resins with epoxy-stopped silicone fluids. In particular, good results are obtained with formulations consisting of 60% resin/40% fluid, epoxy equivalents weights > 1000, where the resin includes at least 5 parts of $M^E + M$ per 100 parts (D or T or D + T) + Q.

20 While there has been described what at present are considered to be the preferred embodiments of the present invention, it will be readily apparent to those skilled in the art that various changes and modifications may be made therein without departing from the invention and it is intended in the appended claims to cover such changes and modifications as fall within the true spirit and scope of the invention.

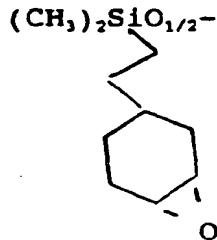
Claims

- 25 1. An ultraviolet radiation-curable epoxysilicone composition comprising a blend of epoxy-functional silicone resins and epoxy-stopped silicone fluids which in the presence of an efficacious amount of 'onium type photocatalyst is curable when exposed to ultraviolet radiation, said blend comprising:
 - 30 (A) from about 80 to about 20 % by weight epoxy-functional silicone resin, said resin containing Q groups, epoxy-functional M groups and at least one member selected from D groups and T groups, at least 5 parts of the sum of M groups and epoxy-functional M groups per 10 parts of the sum of Q groups, D groups and T groups;
 - (B) about 20 to about 80 % by weight epoxy-stopped silicone fluids containing epoxy-functional M groups; and
 35 said blend having an epoxy equivalent weight of greater than 1000.
2. An ultraviolet radiation-curable epoxysilicone composition comprising a blend of epoxy-functional silicone resins and epoxy-stopped silicone fluids which in the presence of an efficacious amount of 'onium type photocatalyst is curable when exposed to ultraviolet radiation, said blend comprising:
 - 40 (A) about 60 % by weight epoxy-functional silicone resin, said resin containing Q groups, epoxy-functional M groups and at least one member selected from D groups and T groups, at least 5 parts of the sum of M groups and epoxy-functional M groups per 10 parts of the sum of Q groups, D groups and T groups;
 - (B) about 40 % by weight epoxy-stopped silicone fluids containing epoxy-functional M groups; and
 45 said blend having an epoxy equivalent weight of greater than 1000.
3. An ultraviolet radiation-curable epoxysilicone composition comprising a blend of epoxy-functional silicone resins and epoxy-stopped silicone fluids curable in the presence of an efficacious amount of photocatalyst and ultraviolet radiation, said blend comprising:
 - 50 (A) about 60 % by weight epoxy-functional silicone resin, said resin containing Q groups, epoxy-functional M groups and at least one member selected from D groups and T groups, at least 5 parts of the sum of M groups and epoxy-functional M groups per 10 parts of the sum of Q groups, D groups and T groups;
 - (B) about 40 % by weight epoxy-stopped silicone fluids containing epoxy-functional M groups; and
 55 said blend having an epoxy equivalent weight of greater than 1000.
4. An ultraviolet radiation-curable epoxysilicone composition comprising a blend of epoxy-functional silicone resins and epoxy-stopped silicone fluids curable in the presence of an efficacious amount of pho-

tocatalyst and ultraviolet radiation, said blend comprising:

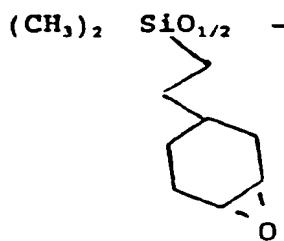
- (A) from about 80 to about 20 % by weight epoxy-functional silicone resin, said resin containing Q groups, epoxy-functional M groups and at least one member selected from D groups and T groups, at least 5 parts of the sum of M groups and epoxy-functional M groups per 10 parts of the sum of Q groups, D groups and T groups;
- (B) about 20 to about 80 % by weight epoxy-stopped silicone fluids containing epoxy-functional M groups; and
- said blend having an epoxy equivalent weight of greater than 1000.

- 10 5. An epoxysilicone composition as in any preceding claim, wherein said epoxy-functional M group is



6. An epoxysilicone as in any preceding claim, wherein the photocatalyst is selected from iodonium and sulphonium salts.

- 25 7. An epoxysilicone as in any preceding claim, wherein the epoxy functional silicone resin has the formula
 $\text{M}^{\text{E}} \text{M}_8 \text{D}_3 \text{T}_2 \text{Q}_5$
 wherein M^{E} comprises:



- 40 M comprises: $(\text{CH}_3)_3\text{SiO}_{1/2}-$
 D comprises: $(\text{CH}_3)_2\text{SiO}-$
 T comprises: $(\text{CH}_3)\text{SiO}_{3/2}-$
 and
 Q comprises: $\text{SiO}_{4/2}-$.

- 45 8. An epoxysilicone composition as in any preceding claim, wherein (B) has an EEW < 8000.
 9. An epoxysilicone composition as in any preceding claim, wherein (B) has an EEW ranging from about 500 to about 2500.

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(54) UV curable epoxysilicones.

(57) A UV curable epoxysilicone blend of an epoxy functional silicone resin containing Q groups, epoxy functional M groups, and at least one member selected from D groups and T groups, at least 5 parts of the sum of M groups and epoxy functional M groups per 10 parts of the sum of Q groups, D groups and T groups ; and an epoxy-stopped silicone fluid containing epoxy functional M groups.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 30 9352

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.5)		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim			
X	EP-A-0 473 995 (GENERAL ELECTRIC) * page 3, paragraph "Component (B)"; page 4, formula; claims *	1-9	C08L83/06		
A	EP-A-0 464 706 (TOSHIBA SILICONE) * claims *	1-9			
A	EP-A-0 449 027 (GENERAL ELECTRIC) * claims 1-12 *	1-9			
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)		
			C08L		
The present search report has been drawn up for all claims					
Place of search	Date of completion of the search	Examiner			
BERLIN	21 March 1995	Hoepfner, W			
CATEGORY OF CITED DOCUMENTS					
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